Toxicology Reports 3 (2016) 644–651

Contents lists available at ScienceDirect

Toxicology Reports

journal homepage: www.elsevier.com/locate/toxrep

Heavy metal content and potential health risk of geophagic white clay from the Kumasi Metropolis in Ghana

Marian Asantewah Nkansah[a,*], Mavis Korankye[a], Godfred Darko[a], Matt Dodd[b]

[a] Department of Chemistry, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana
[b] School of Environment and Sustainability, Royal Roads University, Victoria, BC, Canada

ARTICLE INFO

Article history:
Received 27 April 2016
Received in revised form 19 August 2016
Accepted 19 August 2016
Available online 21 August 2016

Keywords:
Geophagia
White clay
Heavy metals
Health risk assessment
Permitted maximum tolerable daily intake

ABSTRACT

Geophagia is the craving for non-food substances and commonly practiced among pregnant women and children. Consumption of geophagic clay samples can have serious implications on the health of the consumers as a result of the presence of toxic metals such as Pb, As, Hg and Cd. This study sought to determine the levels of heavy metals in the studied geophagic clay samples and to determine the potential risks of heavy metals as cumulative carcinogenic and non-carcinogenic risks to the health of the consumers via oral (ingestion) and dermal exposure routes. A total of thirty (30) white clay samples were analysed using Niton Thermo scientific XRF Analyser (Mobile Test S, NDTr-XL3t-86956, com 24). The clay samples were found to contain essential elements such as Ca, Fe, K and Zn as well as toxic metals such as As and Pb. There were isolated cases of the presence of Hg and all samples had Cd levels below detection. Health risk indices such as hazard quotient and cancer risk were calculated and the results indicated that consumers are likely to suffer from cancer through ingestion of geophagic clay. Bioaccessibility studies were done on zinc and it did not indicate any potential toxicity due to zincs essential nature. The levels of heavy metals in some of the geophagic clay consumed by some residents in the Kumasi were high compared to the Permitted Maximum Tolerable Daily Intake (PMTDI) by (WHO/FAO) and may pose potential health threat over time.

1. Introduction

Geophagia (the deliberate consumption of non-food substances [11] such as ingestion of soil/sand, clay blocks and mud) has been known for centuries. The practice of geophagia has been reported in several countries across continents including Africa (South Africa, Cameroon, Democratic Republic of Congo, Nigeria, Swaziland, Tanzania and Uganda), Asia (China, India, Philippines, and Thailand) and the Americas [20,6]. A variety of reasons for geophagia have been postulated to justify the practice, including religious, cultural, nutritional and medicinal practices, famine, perceived enhancement of personal appearance, pregnancy-related cravings, and enjoyment of the taste, texture or smell of the substance consumed [17]. Geophagy is observed to be more common in pregnant women and children [9,2]. For instance, [17] reported that twenty percent of pregnant women in his study undertaken in Johannesburg were geoghagic, at risk of anaemia and potentially adverse health outcomes. The consumption of geophagic clays can provide benefits such as the ability of clay to absorb dietary and bacterial toxins associated with gastro-intestinal disturbance [6] and free radicals and pesticides from the gastro-intestinal tract. Conversely, geophagia may also expose consumers to toxic or harmful materials such as heavy metals, pathogenic bacteria, viruses and parasites. Heavy metals (As, Se, F and other trace metals) occur naturally in soils during geological processes (weathering and alteration) and anthropogenic activities can also contribute to elevated levels in the soil. Excessive exposure to the harmful heavy metals could lead to one disease or another [31]. A research conducted by [31] revealed that geoghagic clayey soils sold in three major markets (Madina, Makola and Ashaiman) in Ghana contained high levels of As, Pb, Hg, Cd and Co. These results were higher than the WHO/FAO requirement and the levels established by the United States Department of Agriculture. The consumption of these clays by both adults and children could lead to various life threatening diseases. For instance, [24] observed that acute exposure to lead can affect the human central nervous, resulting in dysfunction of the kidney, liver and heart. According to [23], problems of ascariasis is also known to be common among children in Nigeria who practice

* Corresponding author.
E-mail addresses: maan4gr@yahoo.co.uk, mariannkansah@yahoo.com (M.A. Nkansah), mkorankye1988@yahoo.com (M. Korankye), godfreddarko@yahoo.com (G. Darko), matt.dodd@royalroads.ca (M. Dodd).

http://dx.doi.org/10.1016/j.toxrep.2016.08.005
2214-7500/

geophagy. In Tanzania, a survey conducted by [14] reported that geohelminth infection and iron deficiency were observed among pregnant women and HIV infected women who indulge in geophagia. Extreme over indulgence in clay eating can block the colon, which can lead to the perforation and even death. In Ghana, the most patronized geophagic clay is the 'white clay' containing predominantly kaolin [18], particularly sourced from Anfoega in the Volta Region [31]. Several studies have been reported on the mineralogy and microbiology of geophagic clay in sub-saharan Africa including Ghana [5,10,8,21,3]. Heavy metal content of geophagic clayey soil has not been extensively studied in Ghana though geophagia has been practiced for many years.

This study seeks to determine the levels of heavy metals in geophagic white clay samples, their potential risks, cumulative carcinogenic and non-carcinogenic risks via the routes of oral (ingestion) and dermal exposure on the health of consumers.

2. Methodology

2.1. The study area

The Kumasi metropolis lies between latitude 6.35°–6.40° and longitude 1.30°–1.37°. It has an area of about 299 km^2 and elevation of 71 which ranges between 250 and 300 m above sea level. The metropolis is characterized by a tropical wet and dry climate, with relatively constant temperatures throughout the year. The Kumasi metropolis is predominantly a commerce/trade service economy inclusive with an employment level of 71% and this is followed by industry with an employment level of 24%, and agriculture with an employment level of 5%. Kumasi is home to the Kejetia Market otherwise known as the Kumasi Central Market which is the largest in West Africa. It is from this market that most produce are distributed to markets in other regions of the metropolis.

2.2. Experimental procedures

2.2.1. Sampling

A total of thirty (30) pieces of baked ready to eat geophagic white clay samples were randomly obtained from ten (10) markets in the Kumasi Metropolis in the Ashanti region. A total of three (3) samples each were collected from the ten (10) major markets in the meptropolis. These markets are; Abuakwa, Asafo, Asuoyeboah, Ayigya, Bantama, Central Market, Kwame Knrumah university of Science and Technology (KNUST), Kwadaso, Santasi and Tanoso. Pictures of freshly baked clay samples before and after grin have been presented (Figs. 4 and 5).

2.2.2. Sample preparation and analysis

The geophagic clay samples obtained from the markets were dried at room temperature until a constant weight was obtained. Dried clay samples were crushed in turns in a crucible. The crushed samples were then sieved through a 250 μm sieve. The crucible and sieve were cleaned after each sample preparation to avoid contamination. The samples were placed in clean polythene bags, sealed and labelled for easy identification prior to analysis.

2.2.3. Determination of metals in dry powdered white clay by X-ray fluorescence

The heavy metal content in the clay samples were analysed using Thermo scientific Niton XRF Analyser (Mobile Test S, NDTr-XL3t-86956, com 24). The XRF analysis followed the USEPA method 6200 field portable X-Ray Fluorescence Spectrometry for the determination of elemental concentrations of soils and sediments [27]. The equipment was calibrated with reference material OC USGS SAR-M 180–673. The polyethylene sample holder was filled halfway (~3.0 g) with sieved sample. The sample holder was covered with a Mylar film and cupped. The cupped sample was then placed in the XRF shroud and scanned for 180 s to obtain the desired result. All the samples were treated in the same manner.

2.2.4. Wet acid digestion of clay samples

A selection of six (6) of the sieved clay samples were analyzed for total metals after modified aqua regia digestion. An aliquot of 0.5 g sample was added to 3 ml of 1:1:1 $HCl - HNO_3 - H_2O$ mixture. The mixture was digested at 95 °C for 1 h in a heating block. The sample was made to volume with dilute HCl and analyzed by ICP-MS.

2.2.5. Extraction of white clay samples

The extraction protocol was based on the Standard Operating Procedure for an In Vitro Bio-accessibility Assay for Lead in Soil, EPA Method 9200.2-86 [28]. QA/QC included a procedure blank and a laboratory control sample. The sieved clay sample was weighed by difference (1.00 ± 0.05 g) into a 125 ml acid cleaned HPDE bottle. An aliquot of 100 ± 0.5 ml of extraction fluid was measured and added to the bottle. This yielded a sample mass to fluid ratio of 1:100. The pH of the soil/extraction fluid mixture was measured. The extraction solution consisted of 30 g/L glycine (Calbiochem) adjusted to a pH of 1.5 with concentrated HCl (Fisher Scientific, trace metal grade). The bottle was then sealed and placed into the extractor in batches of eight and rotated end-over-end in a 37° ± 2 °C water bath for 1 h. After the extraction was completed, the bottles were removed. Each extract was drawn directly into a disposable 20 ml plastic syringe with a luer slip (National Scientific). A 0.45 μm cellulose acetate filter (25 mm diameter, Cole Palmer) was attached to the syringe and the extract was filtered into a clean 20 ml polyethylene scintillation vial (Wheaton). The filtered extract was stored at 4 °C and subsequently analyzed for metals by ICP-MS.

2.2.6. Analysis for metals in extracts

Metal analysis was conducted with an Agilent Model 7500ce Collision Cell ICP-MS based on United States Environmental Protection Agency (USEPA) SW846 Method 6020A, Inductively Coupled Plasma – Mass Spectrometry, Revision 1 [27].

3. Bioaccessibility calculations

Metal bioaccessibility was calculated as follows:

$$Bioaccessibility, \% = \frac{(Concentration\ in\ extract,\ \mu g/L)\ x\ vol\ of\ extract,\ L}{Concentration\ in\ soil,\ mg/kg\ x\ mass\ of\ soil\ used,\ g} \times 100$$

3.1. Quality control

The XRF analyser was calibrated using certified reference material (OC, USGS, SAR-M AND 180–673) to ensure that the concentrations of the various metals corresponded with the respective concentrations given on the accompanying chart. In order to control the analytical procedure, precision of the analytical results was estimated by replicate analysis.

3.2. Calculation of the average daily intake (ADI)

The amounts of heavy metals consumed were calculated using the average of samples from each location (three each), as indicated in Tables 1a and 1b. The heavy metal content in 70 g is calculated for each location (indicated in Table 2b) and this is used to predict the amount of clay consumed. The values obtained are then compared to the Permitted Maximum Tolerable Daily Intake (PMTDI) recommended by the World Health Organization (WHO) and the Food and Agriculture Organization (FAO).

Table 1a
Concentrations (ppm) of essential metals in geophagic clayey soils.

Sample ID LOD	Ca 3.70	error	Fe 3.30	error	K 3.40	error	Zn 1.80	error
ABU1	366.00	54.78	22103.22	133.94	27672.31	216.84	28.38	4.23
ABU2	174.10	51.68	20473.09	128.79	26049.00	210.99	35.02	4.37
ABU3	131.07	54.42	28870.73	156.89	26463.41	223.21	29.85	4.40
ASA1	377.07	57.27	24191.03	139.54	27831.90	228.93	27.19	4.16
ASA2	352.17	57.42	20738.75	129.11	29129.92	228.93	27.35	4.14
ASA3	204.93	57.90	29975.63	158.38	27220.40	233.98	32.44	4.41
ASY1	208.72	56.39	28354.76	152.66	27731.13	228.89	35.71	4.45
ASY2	152.59	47.77	24601.73	143.57	23614.05	194.94	29.03	4.31
ASY3	237.98	58.21	24427.72	142.44	29705.12	236.51	34.45	4.43
AYI1	100.92	46.62	18878.46	124.88	26267.88	194.28	30.65	4.31
AYI2	178.66	53.28	27086.78	148.85	26106.76	216.72	26.00	4.16
AYI3	171.94	56.31	26611.73	149.09	27109.07	229.14	30.52	4.31
BAN1	165.80	57.36	25315.91	143.84	29358.97	235.50	27.86	4.24
BAN2	165.41	56.65	24575.37	142.09	28891.03	232.30	27.81	4.22
BAN3	279.26	57.78	24618.91	144.32	29680.60	233.14	30.75	4.40
CEN1	50.10	58.47	25890.95	145.88	29279.80	232.93	25.52	4.17
CEN2	165.92	60.42	26675.13	150.08	30289.00	243.40	25.94	4.23
CEN3	147.98	58.66	27931.15	151.95	28435.76	234.62	25.12	4.19
KNU1	249.95	56.29	27501.86	150.66	26895.32	226.38	28.07	4.24
KNU2	188.04	52.94	22368.04	135.22	26686.72	215.82	29.69	4.26
KNU3	198.60	53.01	22417.00	134.54	25981.08	215.16	28.30	4.17
KWA1	183.27	55.20	19816.99	126.01	30777.76	227.33	26.63	4.13
KWA2	257.36	57.70	22401.35	135.56	29521.72	233.82	35.82	4.42
KWA3	124.77	67.37	27179.07	151.56	28154.24	237.22	33.95	4.47
SAN1	163.86	55.27	23004.60	136.32	28133.65	226.56	40.92	4.53
SAN2	159.83	53.23	19395.01	121.10	27094.87	218.38	25.56	3.95
SAN3	218.13	54.03	18591.31	120.36	27831.03	219.79	30.79	4.14
TAN1	116.94	52.45	22242.72	134.77	24861.60	215.26	33.55	4.32
TAN2	267.84	59.25	23904.04	141.87	29790.21	239.24	29.98	4.29
TAN3	247.79	50.70	24877.79	142.97	23292.30	200.45	24.52	4.11
Total	6007.1		728473		829855		897.37	
[a]WHO/FAO	1000		15		3500		20	

ABU = Abuakwa, ASA = Asafo, ASY = Asuoyeboah, AYI = Ayigya, BAN = Bantama, CEN = Central market, KNU = Knustcampus, KWA = Kwadaso, SAN = Santasi, TAN = Tanoso.
[a] WHO/FAO; maximum permissible levels in mg [4].

Table 1b
Concentrations (ppm) of toxic metals in geophagic clayey soils.

Sample ID *LOD*	As *1.80*	error	Pb *1.70*	error	Hg *1.70*	error	Cd *1.90*
ABU1	8.11	2.20	27.70	2.90	<LOD		<LOD
ABU2	9.71	2.14	23.22	2.72	<LOD		<LOD
ABU3	11.07	2.30	26.39	2.93	<LOD		<LOD
ASA1	10.46	2.11	21.35	2.66	5.71	3.64	<LOD
ASA2	8.64	2.20	27.45	2.86	<LOD		<LOD
ASA3	12.45	2.22	21.83	2.74	<LOD		<LOD
ASY1	12.45	2.27	25.53	2.85	<LOD		<LOD
ASY2	8.34	2.16	23.69	2.80	9.75	3.73	<LOD
ASY3	12.31	2.22	22.65	2.72	<LOD		<LOD
AYI1	9.63	2.13	22.01	2.71	<LOD		<LOD
AYI2	13.63	2.27	24.28	2.80	<LOD		<LOD
AYI3	11.71	2.26	24.76	2.83	<LOD		<LOD
BAN1	11.95	2.24	25.01	2.82	<LOD		<LOD
BAN2	10.08	2.21	25.46	2.82	<LOD		<LOD
BAN3	9.36	2.27	26.99	2.91	8.72	3.71	<LOD
CEN1	9.12	2.18	24.76	2.82	<LOD		<LOD
CEN2	10.87	2.30	25.99	2.93	<LOD		<LOD
CEN3	14.18	2.25	24.07	2.82	<LOD		<LOD
KNU1	13.81	2.36	27.88	2.94	<LOD		<LOD
KNU2	9.85	2.25	27.45	2.90	<LOD		<LOD
KNU3	9.85	2.20	26.71	2.85	<LOD		<LOD
KWA1	8.34	2.12	24.14	2.76	<LOD		<LOD
KWA2	10.08	2.19	24.59	2.81	<LOD		<LOD
KWA3	9.73	2.16	21.95	2.75	<LOD		<LOD
SAN1	13.30	2.25	24.81	2.79	<LOD		<LOD
SAN2	8.23	2.06	24.38	2.67	<LOD		<LOD
SAN3	8.58	2.23	30.90	2.93	<LOD		<LOD
TAN1	9.79	2.20	26.63	2.85	<LOD		<LOD
TAN2	9.02	2.23	25.85	2.89	<LOD		<LOD
TAN3	11.48	2.20	23.40	2.75	<LOD		<LOD
TOTAL	390.25		751.87		24.18		<LOD

ABU = Abuakwa, ASA = Asafo, ASY = Asuoyeboah, AYI = Ayigya, BAN = Bantama, CEN = Central market, KNU = Knust campus, KWA = Kwadaso, SAN = Santasi, TAN = Tanoso.

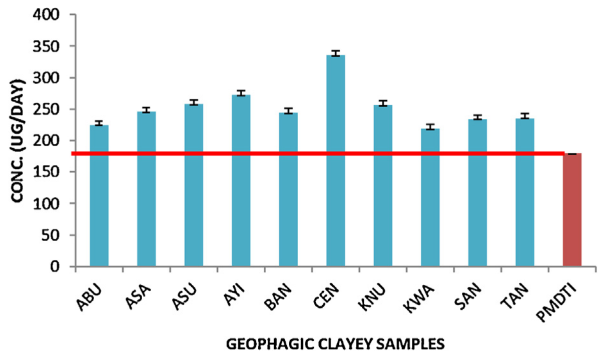

Fig. 1. The mean concentration of arsenic in 70 g of the clay samples compared to Permitted Maximum Tolerable Daily Intake (PMTDI).

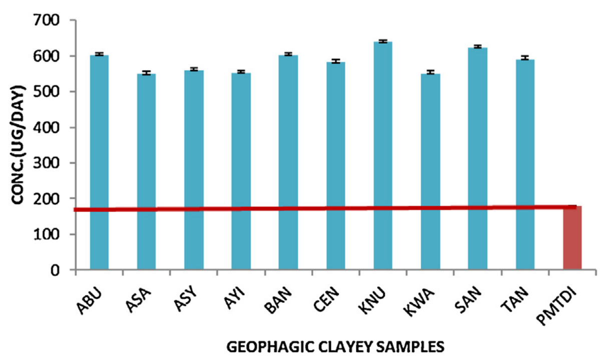

Fig. 2. The mean concentration of lead in 70 g of the clay samples compared to Permitted Maximum Tolerable Daily Intake (PMTDI).

Table 2a
Estimated Standard PMTDI values of heavy metals in 70 g of clay [30,31].

Heavy metals	WHO/FAO PMTDI (ug/kg BW/day)	PMTDI for 60 kg BW(μg/day)
As	3.0	180
Pb	3.0	180
Hg	0.6	36
Cd	0.3	48

4. Results

4.1. Metals levels in white clay

Levels of metals in the clay samples were determined by XRF and ICP-MS analysis. The outcomes have been presented in this section. The concentration of essential metals (Ca, Fe, K and Zn) as well as the toxic metals (As, Pb, Hg and Cd)

4.2. Permitted maximum tolerable daily intake

A research conducted by and [29] indicate that 28% of women of reproductive age in Ghana who practice geophagia consume a daily average of 70 g of clay (Wood and Hackman 2014). The assumption that the average pregnant woman consumes 70 g of clay daily has been used in the determination of the Permitted Maximum Tolerable Daily Intake (PMTDI) by (WHO/FAO) for the samples in this study. The results have been presented in Figs. 1 and 2.

The standard Permitted Maximum Tolerable Daily Intake (PMTDI) in (ug/kg BW/day) of heavy metals in 70 g of clay estimated by WHO and FAO as indicated in Table 2a [30] was used to calculate the PMTDI for 60 kg BW (μg/day) as indicated in Table 2b and compared with the levels of heavy metals in 70 g of the studied geoghagic clayey samples for a 60 kg adult. These were calculated for the metals in this study and the outcome has been presented in Figs. 1 and 2.

Table 2b
Average levels of heavy metals (ppm) in 70 g of geophagic clayey samples consumed.

Sampling Site	Arsenic ± SD	Lead ± SD
ABU	224.70 ± **6.01**	601.30 ± **7.14**
ASA	245.38 ± **6.89**	549.34 ± **6.98**
ASY	257.44 ± **6.62**	558.98 ± **6.56**
AYI	271.98 ± **7.23**	552.61 ± **5.79**
BAN	244.14 ± **6.85**	662.46 ± **6.22**
CEN	335.76 ± **6.23**	581.93 ± **7.8**
KNU	255.81 ± **6.93**	638.09 ± **6.23**
KWA	218.94 ± **7.02**	549.73 ± **8.71**
SAN	234.18 ± **6.54**	622.92 ± **6.14**
TAN	235.58 ± **7.11**	590.17 ± **7.73**

*Mercury and cadmium were below detection limit in almost all the geophagic clayey samples and are therefore not indicated in this table.

4.3. Health risk assessment

Plain data on the metal content of soil samples obtained from the analysis is insufficient to describe the full risk that may arise from the consumption of geophagic clay by residents in the Kumasi Metropolis. Health risk assessment is necessary to estimate the probability of occurrence of any given probable magnitude of adverse health effects over a specified time period and it is a function of the hazard and exposure [19].

In this study, human health risk models including carcinogenic and non-carcinogenic risks raised by USEPA were calculated. The threshold values proposed by USEPA were employed to assess the potential health risks on the consumers. Currently, there is no agreed limit for acceptable maximum carcinogenic and non-carcinogenic risk levels in Ghana. Health risk assessment was examined via ingestion of soil particles and dermal contact of soil. The chronic daily intake (CDI) was calculated for the different heavy metals that were analysed in geophagic clayey samples using the equations in Table 3a and the detailed explanation for all the parameters are listed in Table 3b.

4.4. Hazard quotient

The hazard Quotient (non-carcinogenic risk) of the different metals in the geophagic clayey samples were calculated. HQ is the ratio of exposure to hazardous substances to the chronic reference dose (RFD) of the toxicant ($mg\,kg^{-1}\,d^{-1}$). A HQ less than 1 ($HQ < 1$) means the exposed population is unlikely to experience obvious adverse effects; whereas a HQ above 1 ($HQ > 1$) means there is a chance of non-carcinogenic effect, with an increasing probability as the value increases [15].

4.5. Cancer risk

Cancer risk represents the probability of an individual lifetime health risk from carcinogens. It is necessary to calculate the cancer risk value to estimate whether the consumers are likely to suffer from cancer and this can be evaluated from equation.

Cancer risk = CDI*SF

Where CDI is the chronic daily intake of carcinogens (mg kg−1 d−1); SF is the slope factor of hazardous substances (mg kg−1 d−1).

4.6. Chronic daily intake

The chronic daily intake for the various toxic metals were determined and have been presented in Table 4a.

Table 3a
Defining equations of daily intake via various exposure pathways.

Medium	Exposure pathway	Calculation formulae
Soil	Ingestion	$CDIingest - soil = \frac{CSoil*IRS*EF*ED*CF}{BW*AT}$
	Dermal contact	$CDIdermal - soil = \frac{CSoil*SA*AF*ABS*EF*ED*CF}{BW*AT}$

*ED = equivalent to average life time (65 years for Ghanaian population); *AT = EF*ED [25,32,15].

Table 3b
Parameters for exposure of metals in soil samples used in the study.

Exposure factors	Unit	Value
Concentration in soil sample (C soil)	mg/kg	–
Exposure frequency (EF)	days/year	365
Exposure duration (ED) for soil	Year	65
*Average time for non-carcinogens (AT) in soil	Days	23725
Body weight (BW)	Kg	60
Exposured skin area: (SA)	cm^2	5700
Adherence factor (AF)	$mg\,cm^{-2}$	0.07
Dermal absorption fraction(ABS)		0.03 (As), 0.001 (other metals)
Units conversion factor (CF)	kg mg-1	10^{-6}

Table 4a
Chronic daily intake (CDI) through ingestion and dermal exposure pathways for toxic metals in geophagic clayey soils.

Metals	Mean conc. (mg/kg)	Chronic daily intake (CDI)	
		Ingestion	Dermal
As	10.55	1.51E-05	1.80E-6
Pb	25.06	3.58E-05	1.43E-7
Hg	0.81	1.16E-06	4.62E-9
Cd	–	–	–

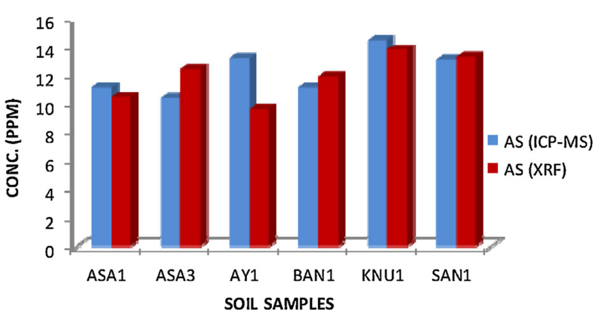

Fig. 3. Relationship between levels of arsenic in soil samples using XRF and ICP-MS techniques.

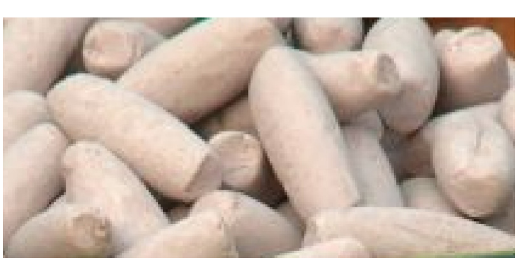

Fig. 4. Freshly baked geophagic clay.

4.7. Comparison between XRF and ICP-MS results for arsenic

A plot on the levels of arsenic in clay samples as determined with XRF and ICP-MS has been presented in Fig. 3. It can be observed that concentrations are approximately the same for samples ASA1, BAN1, KNU1 and SAN1. Samples ASA3 and AY1 however had inconsistent arsenic levels from the two methods; though ICP-MS is known to generally give very low LOD values and gives high accuracy of results [12].

Fig. 5. Powdered geophagic clay.

4.8. Bio-accessibility of zinc

Evaluation of bio-acessibility of metals offers some insight into the amount of contaminant (metal) that is mobilized from the solid matrix (eg. soil) in the human gastrointestinal tract that becomes available for intestinal absorption. In this study, bio-accessibility was performed for only zinc. The% zinc bio-accessibility for geophagic samples from some selected markets have been presented in Table 6.

5. Discussion

5.1. Concentration of toxic metals

From the results, the levels of arsenic in the geophagic clay samples from selected markets in the Kumasi Metropolis ranged from 8.11 to 14.18 ppm (Table 1b) which is higher than the mean exposure level (3.0 μg/kg BW/day) fixed by the Joint FAO/WHO Expert Committee on Food Additives [30]. Ingestion of large amounts of arsenic can lead to gastrointestinal symptoms such as severe vomiting, disturbances of the blood and circulation systems, damage to the nervous system, and eventually death [16].

The levels of lead in 70 g of geophagic clay samples from the selected markets in the range (549.34–622.92 μg) (Table 1b) is over three times the required daily intake for an adult of 60 kg weight as indicated in Fig. 2. Consumption of the clayey samples over a long time can result in serious health effects such as the dysfunctioning of the kidney, liver and heart of the consumers. High concentrations of lead can result in coma, seizure and even death Bonglaisn et al., 2011. Lead targets multiple organs in the body due to its systemic toxicity which can cause cardiovascular, renal, gastro-intestinal and haematological effects [16]. Data from the European Food Safety Authority (EFSA) have related exposure to Pb to effects like neurotoxiicity, carcinogenicity and reproductive failures in adults [13].

Cadmium and mercury were absent in all the samples collected for the study because the concentration was below the lower limit of detection with the exception of samples from ASA1, ASY2 and BAN3 which had values of 5.71 ± 3.69, 9.75 ± 3.73 and 8.72 ± 3.71 respectively for mercury.

5.2. Concentration of essential metals in geophagic white clayey samples

Analysis of the clayey samples obtained from the different markets showed the presence of essential metals. Essential metals such as zinc, copper and iron are nutritionally useful for metabolism and growth. They also form an integral part of one or more enzymes involved in metabolic or biochemical process in the body. The levels of the metals in the geophagic clay were compared with the maximum permissible values set by WHO/FAO. The levels of calcium in the analysed clayey samples were found below the permissible level of 1000 ppm set by WHO/FAO. There were noticeably high levels of potassium (K), iron (Fe) and zinc (n) in the geophagic clayey samples. The high levels of the essential metals can cause serious health problems to consumers. According to [17], high concentration of iron in geophagic clayey samples can result in anaemia among pregnant women and children.

5.3. Significance of the calculated permitted maximum tolerable daily intake (PMTDI)

Permitted Maximum Tolerable Daily Intake is considered as the safe intake levels for an adult of normal weight who consumes an average daily amount of a substance. Geophagic clayey samples from the selected markets in the Kumasi Metropolis had PMDI values higher than the 180 μg value stipulated for a 60 kg adult as indicated in Figs. 1 and 2. The highest concentration was found in samples from the Kumasi Central Market. Exposure to high levels of arsenic can have serious adverse effects on the health of the consumers in the Metropolis. Ingestion of clayey samples of high concentration of arsenic during pregnancy can cause complications in the development of the foetus, especially creating an impact on the optimal brain development. This can lead to impairment of behaviors and skills; including cognitive abilities and social competence that are further developed and fine-tuned during childhood and adolescence. High concentrations can result in skin and lung cancer, and can adversely affect the peripheral nervous system. The PMTDI for the toxic metals in this study was lower than the values reported by [31] in geophagic clayey samples from three major markets in Ghana sourced from Accra, Anfoega, Abidjan and Nigeria.

5.4. Hazard index determined from hazard quotients

Exposure to two or more pollutants may result in additive and/or interactive effects [1,33]. Therefore the hazard index of heavy metals in the soil samples from Suame Magazine industrial area was treated as the arithmetical sum of the hazard quotient of the individual metals.

Table 4b
Reference doses (RFD) mg kg^{-1} day^{-1} for heavy metals used in the study.

Heavy metals	Reference Doses (RFD)
Cu	4.0E-2
Cd	1.0E-3
Zn	3.0E-1
As	3.0E-4
Pb	3.5E-3
Fe	7.0E-1

Chauhan and Chuahan (2014) [7].

Table 4c
Hazard quotient through ingestion and dermal exposure pathways for toxic metals in geophagic clayey soils.

Metals	HQ ingestion	HQ dermal
As	5.03E-02	6.01E-3
Pb	1.02E-2	4.08E-5
Hg	3.86E-2	1.54E-5
Cd	*	*

*Meanstheconcentration < LOD.

$$HIingest = HQAs + HQPb + HQHg$$

$$HIdermal = HQAs + HQPb + HQHg$$

From the individual hazard quotients calculated for the individual metals all the HQ values obtained were less than 1, an indication of no cancer risk. Upon calculation of the hazard indices of heavy metals through ingestion and dermal contact, 0.064 and 0.0006 were obtained respectively, an indication that the consumers are unlikely to experience any adverse effects. Although the hazard index (HI) is less than unity (1), their cumulative effect is of concern. It can be estimated that the overall non-carcinogenic risk assessment on the health of consumers within the Kumasi Metropolis indicated more risk via the ingestion route (HI = 0.064). The results of theis study are however lower than what was reported by [15] on a number of vegetables. The following hazard index vales were obtained; HI > 1 (3.07, 3.67, 1.4, 2.69, 1.74) for rape, celery, cabbage and Asparagus lettuce respectively.

5.5. Cancer risk

The value of cancer slope factor (SF) was assessed in the integrated information risk system (IRIS), provided by USEPA database [26].

Of the six metals investigated, only As and Cd have the potential of inducing both non-carcinogenic and carcinogenic risk, while Pb has the potential of inducing only non-carcinogenic risk. In the case of mercury very sparse data is available on its carcinogenicity. It is necessary to calculate the cancer risk value to estimate whether the consumers within the Kumasi Metropolis are likely to suffer from cancer. The results show cancer risk of 2.26E-05 and 2.69E-06 for arsenic as indicated in Table 5 which are higher than the tolerable level (1E-06 to 1E-04) [25,15]. Therefore, As appears to be the main contaminant with the potential to cause cancer among these heavy metals and the dominating exposure route for As to consumers is by ingestion (oral).

5.6. Implications of the calculated chronic daily intake (CDI)

The degree of toxicity of heavy metal to humans depend on their daily intake. [7]. From the results the CDI ingest-soil, CDI dermal-soil, HQ ingest-soil and HQ dermal-soil for the individual metals

Table 5
Cancer risk for ingestion and dermal exposure pathways for clayey soils.

Metal	CDI ingestion	CDI dermal	(SF)	Ingestion-soil	Dermal absorption – soil
As	1.51E-05	1.80E-6	1.49	2.26E-05	2.69E-06
Cd	*	*	*	*	*

*Means the concentration < LOD.

Table 6
Data on bio-accessibility of Zinc.

Sample ID	Weight used for Extraction (g)	Zinc in soil (mg/kg)	Zinc in extract (mg/L)	Zinc Bioaccessibility (%)
ASA1	1.0214	3.90	24	60.2
ASA3	1.0382	14.1	120	82.0
AY1	1.0053	3.00	21	69.6
BAN1	1.0084	4.00	17	42.1
KNU1	1.0472	5.60	35	59.7
SAN1	1.0326	11.80	35	28.7

were found to be less than unity (CDI < 1) as shown in Tables 4a–c indicating residents in the Kumasi Metropolis would not experience any significant health risk.

5.7. *Significance of bio-accessibility of zinc*

The high% Zinc bio-accessibility in the geophagic clay samples (ASA1, ASA3, AYI1 and KNU1) are in the range (28.7–82.00) % (Table 6) and can be explained by the hydrolysis of zinc at low pH resulting in high solubilisation. The lower% bio-accessibility of Zn in samples BAN1 and SAN1 (below 50%) indicate the adsorption of the zinc metals on the walls of the bottle leading to low affinity of the Zinc metals to the glycine in the remaining extract. The high% Zinc bio-accessibility may not pose any health implications since it is considered an essential element for the growth of organisms.

Zinc is present in all body tissues and fluids and involved in numerous aspects of cellular metabolism. It was estimated that about 10% of human proteins potentially bind zinc, in addition to hundreds, which transport zinc. It is required for the catalytic activity of more than 200 enzymes and it plays a role in immune function, wound healing, protein synthesis, DNA synthesis and cell division. Zinc ions are effective antimicrobial agents even at low concentrations [22]. Cells in the salivary gland, prostate, immune system and intestine use Zn signaling as one way of communicating with other cells. It also can be a neurotoxin; suggesting zinc homeostasis plays a critical role in normal functioning of the brain and central nervous system. Zinc is required for proper sense of taste and smell and supports normal growth and development during pregnancy, childhood, and adolescence. It is believed to possess antioxidant properties, which may protect against accelerated aging and helps speed up the healing process after an injury; however, studies differ as to its effectiveness [22].

6. Conclusion

Geophagic white clay soils sold in some selected markets within the Kumasi metropolis contain essential nutrients such as potassium, iron, calcium and zinc; and toxic metals such as arsenic, lead and mercury. The presence of these metals in the clay could be due to natural occurrence and human activities such as handling and or the baking process. The estimated levels of heavy metals in 70 g of the geophagic clay consumed by some residents in the Kumasi were high compared to the Permitted Maximum Tolerable Daily Intake (PMTDI) by (WHO/FAO). The consumption of these clays by adults and children over a long time poses a potential health threat due to the likelihood of bioaccumulation. These high levels of toxic metals render the clay unwholesome for human consumption.

Acknowledgement

The authors are grateful to Prof. Matt Dodd of the School of Environment and Sustainability of Royal Roads University-Victoria BC, Canada for the provision of the equipment for the analysis of samples in this study.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.toxrep.2016.08.005.

References

[1] O. Akoto, E. Bismark, F. Darko, E. G. and Adei, Concentrations and health risk asessments of heavy metals in fish from the fosu lagoon, Int. J. Environ. Res. 8 (2) (2014) 403–410.
[2] D. Alexander, D. Richardson, L.P. Odom, K. Cromwell, D. Grant, M. Myers, E. Cadet, A.H. Mahama, V. Rangari, D.R. Pace, R. Ankumah, A.K. Kpomblekou, C.A. Fluker, The biological consequences of kaolin geophagia, Prof. Agric. Workers J. 2 (3) (2015) 1–14.
[3] K. Ano Debrah, G. Bruce- Baiden, Microbiological characterization of dry white clay: a pica element in Ghana, Rep. Opin. 2 (6) (2010) 77–81.
[4] T. Belayneth, Z. Atnafu, A. Madhusudhan, Determination of the levels of essential and non-essential metals in rice and soil samples, Int. J. Mod. Chem. Appl. Sci. 2 (1) (2015) 65–72.
[5] M.A. Bisi-Johnson, C.L. Obi, G.E. Ekosse, Microbiological and health related perspectives of geophagia: an overview, Afr. J. Biotechnol. 9 (19) (2010) 5784–5791.
[6] J.N. Bonglaisin, C.M.F. Mbofung, D.N. Lantum, Intake of lead: cadmium and mercury in kailon eating: a quality assessment, J. Med. Sci. 11 (7) (2011) 267–273.
[7] G. Chauhan, U.K. Chauhan, Human health risk assessment of heavy metals via dietary intake of vegetables grown in wastewater irrigated area of Rewa, India, Int. J. Sci. Res. Publ. 4 (9) (2014) 1–9.
[8] G.E. Ekosse, D.N. Jumbam, Geophagic clays: their mineralogy, chemistry and possible human health effects, Afr. J. Biotechnol. 9 (40) (2010) 6755–6767.
[9] E. Fosso-Kankeu, F. Waanders, E.T. Ubomba-Jaswa, K. Abia, Identification of metals in geophagic clays: investigation of their behaviour in simulated gastric fluid, in: 7th International Conference on Latest Trends in Engineering & Technology (ICLTET'2015), Pretoria, South Africa, 2015, pp. 49–53.
[10] J.M. Gichumbi, O. Ombaka, J.G. Githaiga, Chemical and mineralogical analysis of geophagic materials consumed by pregnant women in eastern nairobi and nyanza provinces in Kenya, Sacha J. Environ. Studies 1 (1) (2011) 116–122.
[11] J.M. Gichumbi, J.K. Maghanga, E.C. Cheshari, R.O. Ongulu, J.G. Gichuki, Comparison of chemical and mineralogical properties of geophagic materials from taita and mombasa, Kenya, Int. J. Sci. Eng. Res. 3 (10) (2012) 1–7.
[12] J.M. Guthrie, Overview of X-Ray Fluorescence, 2012, http://archaeometry.missouri.edu/xrf_overview.html (accessed: 10.06.16).
[13] M. Herreros, S. Inigo-Nunez, E. Sanchez-Perez, T. Encinas, A. Gonzalez- Bulnes, Contribution of fish consumption to heavy metals exposure in women of childbearing age from a mediterranean country (Spain), Food Chem. Toxicol. 46 (2008) 1591–1595.
[14] K. Kawai, E. Saathoff, G. Antelman, G. Msamang, W.W. Fawzi, Geophagy in relation to anemia and helminths infections among HIV infected pregnant women in Tanzania, Am. J. Trop. Med. Hyg. 80 (1) (2009) 36–43.

[15] X. Liu, Q. Song, Y. Tang, W. Li, J. Xu, J. Wu, F. Wang, Human health risk assessment of heavy metals in soil–vegetable system: a multi-medianalysis, Sci. Total Environ. 40 (2013) 530–540.
[16] M. Mahurpawar, Effects of heavy metals on human health, Int. J. Res. Granthaalayah (2015) 1–7.
[17] A. Mathee, N. Naicker, T. Kootbodien, T. Mahuma, P. Nkomo, I. Naik, T. De Wet, A cross-sectional analytical study of geophagia practices and blood metal concentrations in pregnant women in Johannesburg, South Africa, S. Afr. Med. J. 104 (8) (2014) 568–573.
[18] F.W.Y. Momade, S.K.Y. Gawu, Geochemical and mineralogical characteristics of Lithomargic clay, J. Sci. Technol. 29 (2) (2009) 96–106.
[19] M.Z.H. Naveedullah, Y. Chuuna, S. Hui, D. Dechao, S. Chaofeng, L. Liping, C. Yingxu, Concentrations and health risk assessement of selected heavy metals in surface water of the siling reservoir watershed in Zhejiang Province, China, Polish J. Environ. studies 23 (3) (2014) 801–811.
[20] V.M. Ngole, G.E. Ekosse, L. De Jager, S.P. Songca, Physicochemical characteristics of geophagic clayey soils from South Africa and Swaziland, Afr. J. Biotechnol. 9 (36) (2010) 5929–5937.
[21] V.M. Ngole, G.E. Ekosse, Physico-chemistry, mineralogy geochemistry and nutrient bioaccessibility of geophagic soils from Eastern Cape, South Africa, Sci. Res. Essays 7 (12) (2012) 1319–1331.
[22] J. Osredkar, N. Sustar, Copper and zinc, biological role and significance of copper/zinc imbalance, J. Clin. Toxicol. (2011) 1–18.
[23] U.C. Ozumba, N. Ozumba, Patterns of helminth infection in the human gut at the University of Nigeria Teaching Hospital, Enugu, Nigeria, J. Health Sci. 48 (2002) 263–268.
[24] O. Selinus, R.B. Finkelman, J.A. Centeno, Medical Geology. A Regional Synthesis, Pub. Springer, 2010, pp. pp. 88.
[25] USEPA, Risk Assessment Guidance for Superfund: Volume 3—Part A, Process for Conducting Probabilistic Risk Assessment, US Environmental Protection Agency, Washington, DC, 2001 (EPA 540-R-02-002).
[26] USEPA, Risk Assessment Guidance for Superfund. Volume I: Human Health Evaluation Manual—Part E, Supplemental Guidance for Dermal Risk Assessment, Office of Superfund Remediation and Technology Innovation, Washington, DC, 2004 (EPA/540/R/99/005. OSWER 9285. 7-02EP PB99-963312).
[27] USEPA, Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment Method: 6200, 2007, https://www.epa.gov/sites/production/files/2015-12/documents/6200.pdf (accessed: 10).06.16).
[28] USEPA, Standard Operating Procedure for an In Vitro Bioaccessibility Assay for Lead in Soil, 9200, EPA, 2012, pp. 2–86.
[29] F.A. Tayie, G. Koduah, S.A.P. Mork, Geophagia clay soil as a source of mineral nutrients and toxicants, Afr. J. Food Agric. Nutr. Dev. 13 (1) (2013) 7157–7170.
[30] WHO, Food additive and contaminants (Flavours; cadmium and lead, in: Seventy-third Meeting of the Joint FAO/WHO Expert Committee on Food Additives (JECFA), Geneva, 2011, pp. 1–535.
[31] A. Woode, S.F. Hackman-Duncan, Risks associated with geophagia in Ghana? Can. J. Pure.Appl. Sci. 8 (1) (2014) 2789–2794.
[32] X.L. Wang, T. Sato, B.S. Xing, S. Tao, Health risks of heavy metals to the general public in Tianjin, China via consumption of vegetables and fish, Sci. Total Environ. 350 (2005) 28–37.
[33] N. Zheng, Q. Wang, X. Zhang, D. Zheng, Z. Zhang, S. Zhang, Population health risk due to dietary intake of heavy metals in the industrial area of Huludao City, China, Sci. Total Environ. 387 (2007) 96–104.